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ABSTRACT *(Maximum 200 words)*

The current study has examined the influence of supercritical water (SW) on reactions of organic chlorides. The aliphatic compounds were represented by 1-chloro-3-phenylpropane which reacted rapidly and completely by both pyrolysis and with SW. The presence of SW produced only a minor shift in organic products. SW did promote the reaction between the metal walls and the chloride, or HCl formed from it, to quantitatively produce metal chlorides, as confirmed by ICP analysis; after dry pyrolysis some HCl, still remained. However, SW did significantly increase the rate of consumption of the aromatic chloride, 2-chlorotoluene, over that of dry prorolysis; metal chlorides were evident in the water layer and HCl was not detected in the SW reaction. Because the reaction of organic chlorides, and/or the HCl formed from them, with the reactor walls may influence the rates and product distributions, experiments were begun using Vycor inserts to provide a more inert surface. Pyrex was not inert to SW. The results of these experiments, plus those with added $NiCl_2$ or $FeCl_2$ solutions in the Vycor insert, showed conclusively that both the metal wall and the metal salts had a catalytic effect in the reaction. Similar catalysis by the reactor wall was observed for the SW - 4-chlorophenol reaction. These results indicate that organic chlorides can produce a corrosion problem at SW conditions of the metal components of flow systems and with oxide supported catalyst beds.

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DEVELOPMENT OF A GLASS REACTOR LINING FOR CHLOROCARBON-SUPERCRITICAL WATER REACTIONS

FINAL REPORT

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AUGUST 9, 1995

U.S. ARMY RESEARCH OFFICE

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FINAL REPORT

STATEMENT OF THE PROBLEM

A problem that we observed in our results with supercritical water (SW) - chlorocarbon reactions (1,2) which had not been adequately addressed in previous studies (3,4) was the fate of HCl assumed to be formed. In our earlier studies HCl was not found but significant amounts of soluble metal salts were observed. This led to the conclusions that: (a) significant corrosion of the reactor walls (whether Inconel or stainless steel), takes place which may also occur in the entrance lines of flow systems if reaction is initiated there, (b) the HCl may also erode oxide supported catalysts and (c) the chemistry of the chloride-SW reaction may be affected by this wall reaction.

Thus the objective of this one year continuation program was to establish, if possible, the conditions under which a glass ampoule could be used as an insert in the metal reactor. The ampoule would contain the reaction mixture, the metal shell would contain sufficient water to allow pressurization external to the ampoule about equal to that in the ampoule. In this way it is expected that the HCl produced from chlorocompounds will not react with the metal walls, thus providing a different reaction environment and product distribution than when the HCl is converted to H_2 in the metal reactors, and in addition the insert would protect the wall from corrosion.

A secondary consideration was that although supercritical water oxidation (SWO) may

provide a more rapid and complete destruction of hazardous materials, the use of SW alone may provide an alternative to complete destruction that could lead to commercially useful products. We have found that some of the model compounds representing hazardous materials, under the proper conditions, form products in good yields which are of industrial value. A two stage operation could separate these useful products formed in the first stage with SW, followed by SWO of the chars and tars in the second stage.

SUMMARY OF RESULTS

A few preliminary experiments were carried out exposing samples of pyrex, Vycor and quartz to SW. The pyrex showed significant attack by the SW, leaving a soft, white, powdery layer on the surface, whereas the other two appeared unaffected. Thus the Vycor ampoules were constructed of standard 15mm tubing and one was sealed and exposed to temperatures and pressures up to 500^{0}C and 390 bar without rupture.

1-Chloro-3-phyenylpropane (CPP)

CPP was used to represent alkyl chlorides; the CPP was completely consumed at all conditions and the products were very similar from the SW and pyrolysis reactions in metal. However, some differences were observed when the SW reaction was in Vycor, the 118 molecular wt species (isomers of dihydroindene, methylstyrene, etc.) were absent and a wider variety of dipehenyl alkyl species, from C_3 to C_6's were found; higher yields of tar were obtained also. It is interesting to note that a large fraction of the products' sidechains were saturated, indicating that hydrogen was either reducing the double bonds formed from HCl elimination or was reacting with a radical formed from a C-Cl rupture. The data indicates that much of the hydrogen may be formed by reactions with the metal walls. The metal ion concentrations in the water layer were

determined by ICP analysis and show an amount about equivalent to the CPP. Thus, the reactant, or any HCl formed, reacted with the metal walls to form metal chlorides which dissolved in the water layer on cooling. The addition of CaO did reduce the HCl attack on the metal walls but did not eliminate it. ICP analysis showed only trace amounts of metal ions in the water layers from reactions when chlorine was absent.

2-Chlorotoluene (CT)

The most interesting results were obtained with CT. The data show that SW had a very significant effect on the rate of consumption of CT, increasing extents of reaction at 450°C from only about 10% up to 80 to 100% at the same reaction times. Thus, the presence of SW does facilitate the removal of aromatic chlorine at a lower temperature (450°C), where less char and tar are formed, to produce good yields of toluene. At 500°C more C-C bond rupture took place increasing char/tar and benzene yields at the expense of those of toluene. However, the results of the experiments with Vycor inserts show that these increases in extents of reaction in the SW experiments are promoted, both directly and indirectly, by the metal walls. The extents of reaction with added $NiCl_2$ and $FeCl_2$ show that these have a catalytic effect on CT consumption; however, these extents are still less than those obtained directly in the metal reactor, indicating that both metal salts and metal walls are catalysts. This catalytic effect appears to be considerably reduced in the absence of SW, but still present, as indicated by extents of reaction at 500°C without water and that at 495°C with SW in Vycor.

4-Chlorophenol (4CP)

A brief examination of 4 CP indicated a similar behavior to that of CT, although it was somewhat more reactive. Again the catalytic effect of metal walls and/or salts was evident.

CONCLUSIONS

From the results of these experiments the following can be concluded:

(a) Organic chlorides will react quantitatively either directly or indirectly through HCl formed from them, with the metal walls of the reactor at SW conditions forming metal chlorides. This reaction would be expected in the entrance lines of flow systems, if sufficiently heated, and with metal catalysts and/or their supports.

(b) Vycor or quartz inserts can protect the heated metal components of the reactor systems, but not oxide supported catalyst beds. Pyrex appears unsatisfactory since it is not inert to SW.

(c) The use of Vycor inserts decreases the rates of reaction (in the absence of oxidizers) of aromatic chlorides in SW drastically; both the metal walls and the salts formed from them act as catalysts for the reaction and this catalysis is apparently promoted by the presence of SW.

PUBLICATIONS

1. "The Removal of Organic Heteroatoms by Supercritical Water", T.J. Houser and X. Liu, proceedings of the 3rd International Symposium on Supercritical Fluids, October 1994, Strasbourg (France), vol. 3, p. 75.

2. "Reactions Involving Supercritical Water and Organoheteroatoms", T.J. Houser and X. Liu, presented at the 1994 Annual Meeting of A.I.Ch.E., November 1994, San Francisco, CA.

3. "The Destruction of Selected Hazardous Compound Using Supercritical Water", T.J. Houser, Y. Zhou and X. Liu, submitted to J. Supercritical Fluids.

4. "Reactions of 1-Chloro-3-phenylpropane, 2-Chlorotoluene and 4-Chlorophenol in Supercritical Water", T.J. Houser and X. Liu, submitted to J. Supercritical Fluids.

PARTICIPATING SCIENTIFIC PERSONNEL

Supported personnel:

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Previous Students:

Ying Zhou - M.S. Graduate Student

Xu Liu - M.S. Graduate Student

These students have not completed their theses, thus degrees have not been granted.

REFERENCES

1. T.J. Houser, Y. Zhou, C-C. Tsao and X. Liu, ACS Symposium Series No. 514, Supercritical Fluid Engineering Science Fundamentals and Applications, Eds. E. Kiran and J.F. Brennecke, 1993, pp. 328-337.

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